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SULPHUR ISOTOPE INVESTIGATION OF THE
QUEMONT ORE DEPOSIT

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY

by

GERALD J. RYZNAR B.Sc.

EDMONTON, ALBERTA

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UNIVERSITY OF ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Sulphur Isotope Investigation of the Quemont Ore Deposit", submitted by Gerald J. Ryznar, B.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Sulphur isotope ratios S^{32}/S^{34} were determined for 43 sulphide samples from a massive sulphide deposit in the Quemont Mine at Noranda in northwestern Quebec. Most of the samples were burned directly to SO_2 . The sulphur isotope ratios were determined with a gas source, simultaneous collecting 12 inch 90° magnetic analyzer mass spectrometer. S^{32}/S^{34} ratios were determined for twenty-one samples of pyrite, nine samples of pyrrhotite, seven samples of sphalerite and six samples of chalcopyrite. All ratios are expressed in δ values, that is parts per thousand (0/00) above or below the meteoritic value for S^{32}/S^{34} .

The average values for the S^{32}/S^{34} ratios of all the samples showed an extremely tight grouping about the meteoritic value. The spread of values was from 0 to +1.8 δ units indicating derivation from the mantle or a source in direct contact with the mantle. Results showed that in all cases except two, the chalcopyrite and the sphalerite were enriched in the lighter isotope of sulphur (S^{32}) with respect to the pyrite and pyrrhotite. This follows the normal paragenetic sequence of pyrite, pyrrhotite, sphalerite and chalcopyrite and indicates Rayleigh fractionation due to crystallization of different mineral species from a melt. All samples from the southwest ore body of the mine showed an enrichment of the heavy isotope (S^{34}) with depth. This phenomenon is believed to be a result of the emplacement of an intrusive body close to the ore, causing differential migration of the light sulphur isotope (S^{32}) away from the source of heat. This is evidence that the intrusive below the southwest ore body is post-ore.

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INTRODUCTION

Extensive research has been carried out in the sulphur isotope field in the last few years. Since the early work of Thode, MacNamara and Collins (1949) and of MacNamara and Thode (1950) the amount of research in this field has increased rapidly so that at present there is a large quantity of data available. Although a number of problems concerning sulphur isotope abundances have been solved, we are still at the stage where our capability of using our knowledge of sulphur isotopes as a tool in solving further geological problems is still quite limited.

The investigation undertaken for this thesis consisted of a study of the sulphur isotope ratios in the massive sulphide deposits at the Quemont mine. One zone, the Southwest ore body, was studied in more detail. Measurements of the sulphur isotope ratios of various minerals were made with a gas source mass spectrometer. Hand specimens used in the study were collected at different levels throughout the mine. The minerals for which the sulphur isotope ratios were determined were pyrite, pyrrhotite, chalcopyrite and sphalerite. Emphasis was placed on pyrite and pyrrhotite since these minerals are the predominant minerals of the deposit. The samples used in this study were collected primarily for a study of pyrite and pyrrhotite, and as a result chalcopyrite and sphalerite are not too commonly found in the hand specimens. For this reason sulphur isotope ratios were determined for only a small number of chalcopyrite and sphalerite samples.

This investigation was carried out with the hope that through the observation of the behaviour of the sulphur isotopes within a given ore body, some conclusions might be formed as to its genesis or history.

PREVIOUS WORK

Kulp et al. (1956), Vinogradov et al. (1956) and Jensen (1959) were among the first workers who attempted to use the sulphur isotope ratios of S^{32}/S^{34} to learn something about the genesis of certain sulphide deposits. Vinogradov et al. (ibid) stated that the origin of sulphide deposits can be determined through the study of sulphur isotopes. Jensen (ibid) classified hydrothermal deposits into magmatic hydrothermal, metamorphic hydrothermal, and ground water hydrothermal. He showed that to some extent deposits grouped under each of these sub-divisions showed similar sulphur isotope characteristics. His characteristics were based on the range of values of the S^{32}/S^{34} ratios. Magmatic hydrothermal deposits were characterized by a small range of values, metamorphic hydrothermal by a large range of values and ground water hydrothermal were characterized by a large range of values and always enriched in the light isotope (S^{32}). Although these criteria seem rather broad and do show some overlap, they may be of some aid when the genesis of an ore deposit is under consideration.

Other workers have also used sulphur isotope ratios as an aid to the interpretation of certain geological problems. Thode, Dunford, and Shima, (1962) used sulphur isotope ratios as added evidence to show that the Sudbury intrusive was a single intrusive sheet which subsequently had undergone some gravity differentiation. They also used the sulphur isotope ratios to point out that the majority of the Sudbury ores were very closely related to the norite, except for some deposits in the centre of the basin within the Whitewater series, which were considered to be of hydrothermal origin.

Jensen (1957) after a study of sulphur isotope ratios in individual hand specimens, suggested that S^{32}/S^{34} ratios may be a valuable aid in interpreting mineral history with respect to source of mineralizing solutions, changes in temperatures and replacement or the mechanics of solid solution.

Dechow (1960) has apparently followed up some of Jensen's suggestions, and has presented his ideas on the formation of the Heathe Steele ore deposit of New Brunswick. Since the ore deposits are enriched in the heavy isotope he advocated as the source, a granitized body of sediments from which the ore was derived by magmatic hydrothermal solutions. By assuming certain values of sulphur isotope ratios for sulphides and sulphates under equilibrium conditions, he calculated the equilibrium constant for the exchange reaction. From this he in turn calculated the temperature at the time of the exchange. This temperature turned out to be eight hundred degrees centigrade. Since the ratios of the sulphides in the nearby granites were very similar to the ratios obtained from the ore deposit, Dechow postulated that the granite was the source of the ore. Dechow's work is one of the few studies done on individual deposits and shows the type of information which may be obtainable through a study of the sulphur isotope ratios.

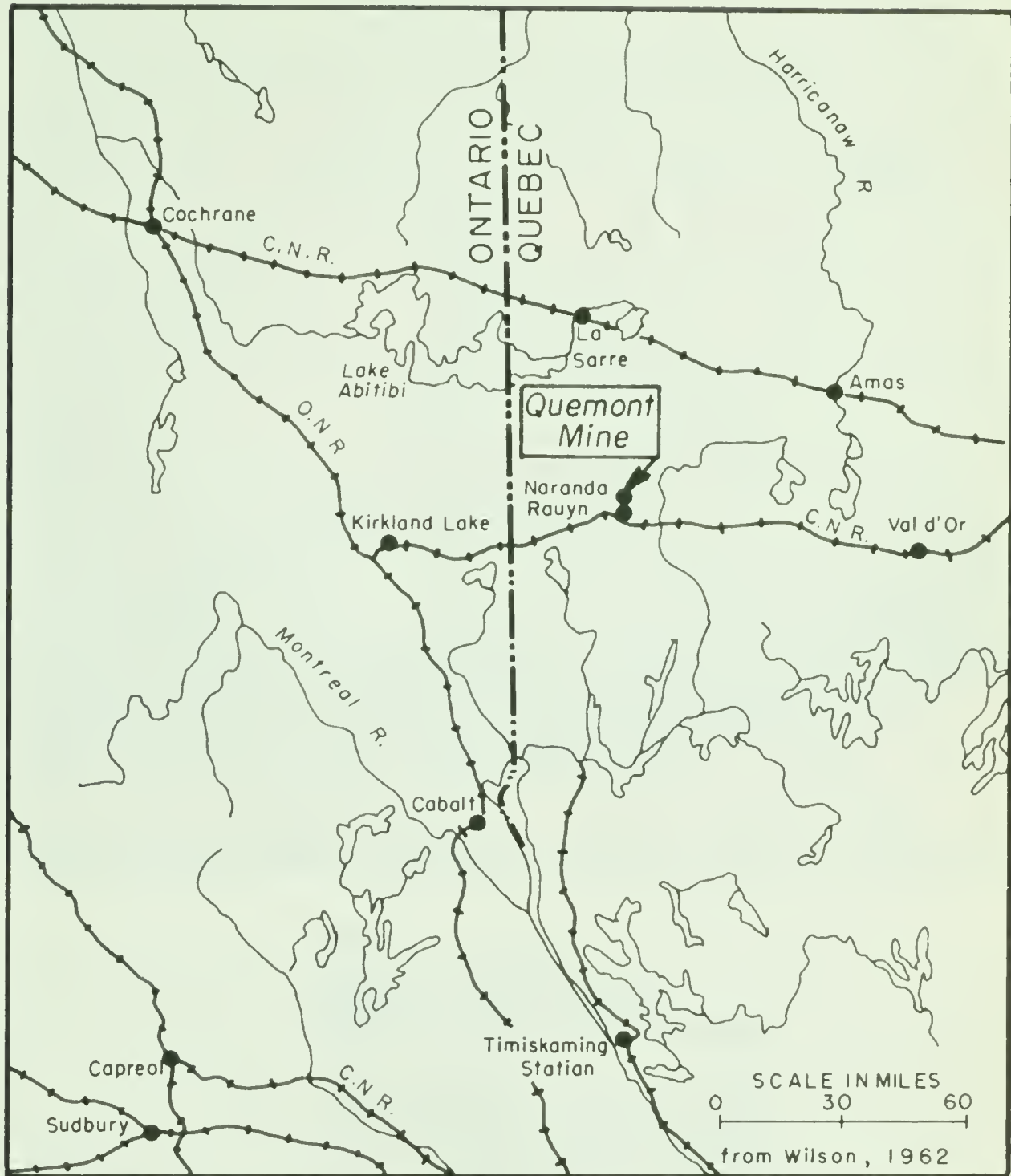
Jensen (1958), presented a hypothesis for the origin of sandstone-type uranium deposits, following a study of their S^{32}/S^{34} ratios. He stated that the high ratios are immediately suggestive, although not diagnostic, of sulphur derived from hydrogen-sulfide of organic origin. The widespread in the values of both closely spaced organic hydrogen sulphide samples and juxtaposed sedimentary sulphides led him to believe that the sulphides were formed through the reaction of organic hydrogen sulphide and iron sulphate with the release of the heavy sulphate ion to the sea.

The values Jensen obtained for the ratio of S^{32}/S^{34} in the sandstone-type uranium deposits had a very wide range with the majority of the values between a S^{32}/S^{34} ratio of 22.80 and 23.32. This corresponds approximately to values of -26.5 S units to -50 S units.

Bateman and Jensen (1956) studied sulphur isotope ratios of the Rhodesian copper deposits in an attempt to determine whether they were syngenetic or epigenetic deposits. Because work was done only on a small number of samples, and there was no

apparent continuity in the sulphur ratios obtained, no conclusions were reached as to the origin of the deposits. The authors did recommend that further work be done on the problem.

Tupper (1960), another of the recent workers with sulphur isotopes, studied the sulphur isotopes of the Bathurst–Newcastle area of New Brunswick. From this investigation he concluded that these massive sulphide ore deposits were derived from well homogenized magmatic hydrothermal solutions.



Map showing location of Quemont Mine

Figure 1.

General Geology of the Noranda Area



PROTEROZOIC

 COBALT GROUP
conglomerate, greywacke

ARCHEAN

 ACID INTRUSIVE ROCKS
granites and granodiorite

TIMISKAMING

 CADILLAC GROUP
sediments, minor volcanics

KEEWATIN

 ABITIBI GROUP
volcanic rocks

 PONTIAC GROUP
mica schist, minor volcanic rocks

SCALE IN MILES
0 2 4

Figure 1A.

GEOLOGY

Geology of the area

The Quemont mine is situated in Noranda, Quebec. (Fig. 1). The 810 acre mine property lies north of and adjacent to the property of Noranda Mines Ltd. (Horne Mine) in Rouyn township. A large area of the southern part of the mine property is under the north arm of Osisko Lake (Lac Tremoy).

Geologically, Rouyn township is part of the Timiskaming sub-province which covers a large portion of northwestern Quebec and northeastern Ontario. The geology of the area immediately surrounding the Quemont property is quite similar to the rest of the Timiskaming sub-province (Fig. 1A). For the most part, the bedrock is of Archaen age except for a small area which is underlain by Cobalt sediments. A number of structural breaks occur in the near vicinity of the Quemont Mine (Campbell, 1963). These are (1) the Horne Creek fault which cuts across the southern boundary of the mine property, (2) the Cadillac-Bouzan Lake fault zone which lies some four miles south of the property and (3) the Porcupine-Destor fault zone which lies some sixteen miles north of the Quemont Mine.

Most of the area is underlain by rocks of Keewatin age. These include the rocks of both the Abitibi and the Pontiac groups as designated by Wilson (1956). The Pontiac group consists of those rocks which occur south of the Cadillac-Bouzan Lake fault zone and lie between the Timiskaming sediments and the irregular band of intrusive granites which occur some ten or twelve miles further south. As shown in Fig. 1A, only a small southern portion of the map is occupied by rocks of the Pontiac group.

The Abitibi group consists of the Keewatin lavas and volcanics north of the Cadillac-Bouzan Lake fault zone. The lavas of this group range from intermediate to acid in composition, with the large majority of the flows consisting of various phases of andesite and rhyolite. In a few localities dacite and trachyte are present. The various phases of the andesites and rhyolites include andesite tuffs, andesite agglomerate,

pillow andesites, massive rhyolite, spherulitic rhyolite, rhyolite breccias and rhyolite tuffs. A high sodium content is a noticeable feature of the Abitibi rocks (Wilson, 1952).

The Pontiac group consists predominantly of siliceous mica schist with bands of recrystallized volcanic rock which may originally have been andesite or andesite tuff. (Wilson, *ibid*). Pillow structures in the transformed lavas are still available for top determinations.

Separating the Pontiac group from the Abitibi is a belt of Timiskaming sediments folded into an east-west striking faulted synclorium. The maximum surface width of this belt in the map area is about 12,000 feet. Portions of the synclorium appear on the north side of the Cadillac-Bouzan Lake fault zone, but are discontinuous. The Timiskaming series consists of conglomerate and greywacke. The pebbles and boulders within the conglomerate consist mainly of volcanic rock but there are some granite and a few jasper pebbles present. The Timiskaming overlies the Pontiac and the Abitibi groups with structural unconformity and is in turn overlain by the Cobalt group in the western portion of the map (Fig. 1A).

The Cobalt group is present in Beauchastel township. This is a small eastward extension of the Cobalt sediments which cover a much larger area in the province of Ontario. The sediments of this group consist both conglomerates and greywackes or argillites believed to be of interglacial lacustrine origin. The boulders in the conglomerate exhibit typical characteristics of a glacial deposit. A glacial origin for the sediments was first postulated by Coleman (1908) and since then this hypothesis has received almost unanimous approval. The Cobalt sediments are approximately 1,000 feet thick in Beauchastel township and dip gently to the west.

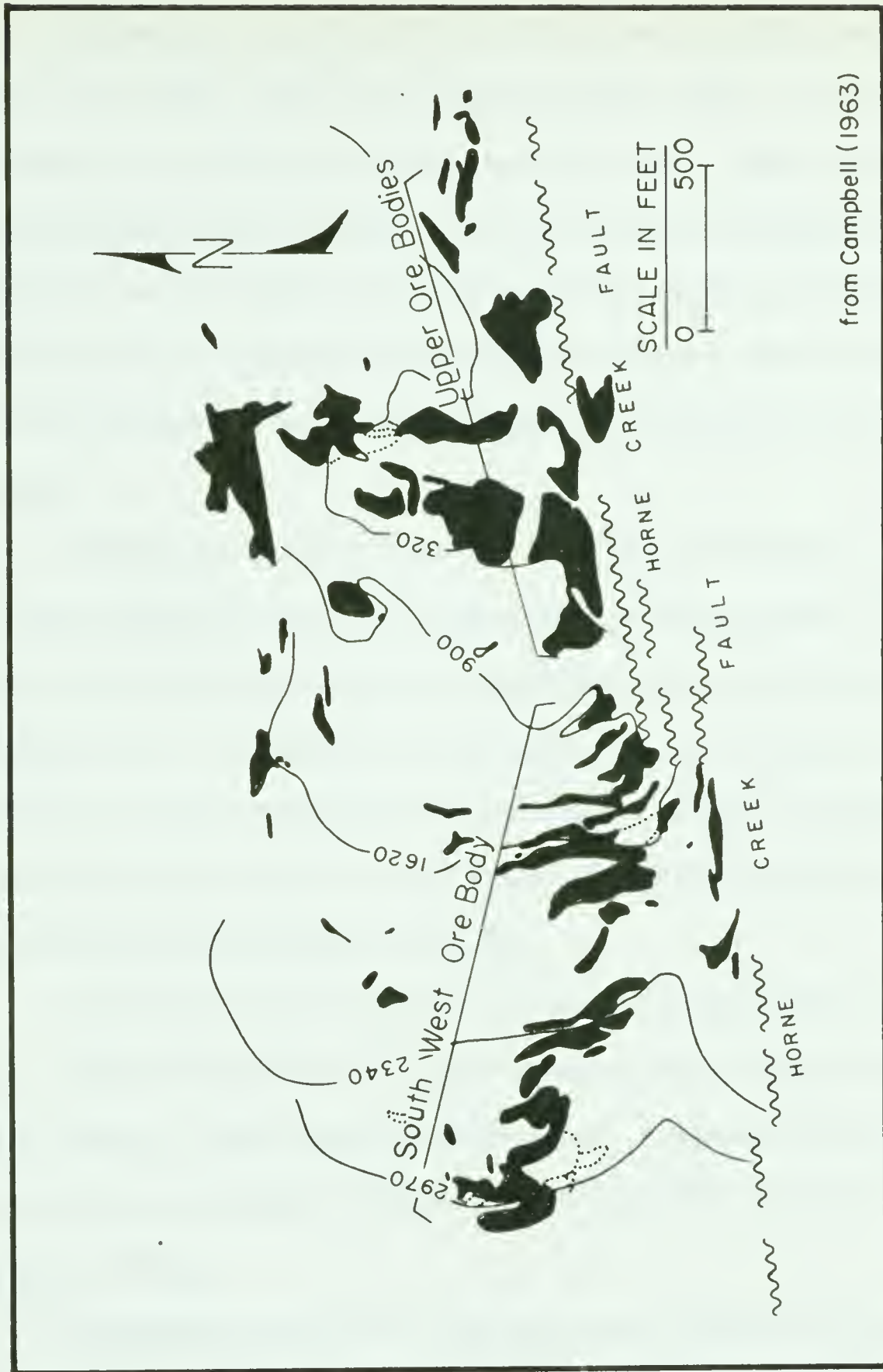
A large variety of intrusive rocks are found in the general area. They include diorite and quartz diorite, syenite porphyry, quartz porphyry, rhyolite, rhyolite porphyry, diabases and gabbros and granites and granodiorites. Albite granite and the granodiorite occur mostly in the centre of the map area (Fig. 1A), with the Powell

granite, the Lake Flavrian granite and the Lake Dufault granodiorite being the main intrusive masses. The granodiorites and the albite granites are considered to be Algomian in age.

As stated previously, a number of major faults occur in the general area of the Quemont Mine. The Cadillac-Bouzan Lake fault (Fig. 1A) is considered a major structural break. It is of considerable importance since it is one of the major factors in localizing a great number of the mineral deposits in the area. The Cadillac-Bouzan Lake fault zone is thought to be the east ward extension of the Larder Lake fault zone in Ontario. Little of the fault is exposed in outcrop but some knowledge of the movement along this fault has been gained from underground mine workings. The fault zone itself is an intensely sheared zone which may be as wide as 500 feet, consisting mainly of talc chlorite schist. Many smaller shear zones branch off from the main break, or run parallel to it. The character and total amount of displacement along the Cadillac-Bouzan Lake fault zone is still undetermined.

The Porcupine-Destor fault zone is another major structural break which runs across northwestern Quebec. It is some sixteen miles distant from the Quemont Mine and therefore not considered to have had any direct effect on the immediate area of the Quemont Mine. The Porcupine-Destor fault zone is not shown in Fig. 1A, but it runs in a north-west direction just off the northeast corner of the map.

The other major structural feature in this area is the Horne Creek fault. It branches off from the Cadillac-Bouzan Lake fault zone in Desserat township in Quebec and extends north-east across Beauchastel township and into Rouyn township. In its full extent it is some twelve to fifteen miles long. It is a composite fault zone showing evidence of repeated movement but total movement along the fault has as of yet not been determined.



from Campbell (1963)

Fig. 1B: Contour map of Quemont Deposit. Contours show footwall of porphyritic rhyolite. Ore is shown in black. Ore bodies as designated in this study are indicated.

Mine Geology

General

The geology of the Quemont Mine has been described previously by Scott (1948), Taylor (1953), (1957) and Campbell (1962), (1963). As seen in Fig. 1A the mine property is underlain by Keewatin volcanic rocks. These consist mainly of rhyolite although a few thin bands of pillowed andesite are present. The rhyolites are present in various phases, including porphyritic rhyolite, rhyolite breccia and rhyolite tuff. The ore occurs in the rhyolite breccia at or near the contact with the porphyritic rhyolite and for this reason these two rock types are the two most important in the mine.

The porphyritic rhyolite is a very fine grained hard dense rock containing small quartz phenocrysts and forms a bed at least 1,700 feet thick. This porphyritic rhyolite overlies the rhyolite breccia conformably. The rhyolite breccia is at least 1,000 feet thick. The fragments in the breccia may be as large as one foot in diameter but the majority of fragments have a diameter of one or two inches. Quartz phenocrysts are rare to absent in the breccia. The breccia fragments are more evident at the contact with the porphyritic rhyolite.

Acid intrusives are common throughout the mine workings, occurring as irregular dykes striking north. The acid intrusives consist of quartz-feldspar porphyry, feldspar porphyry, quartz porphyry and rhyolites. A number of fine grained rhyolite dykes striking approximately N 80° W, with a dip of 85° to the south, are also found in the mine workings.

Metadiabase and diorite intrusives are found mostly in the south part of the mine. Two diabase dykes, one striking east and the other striking north occur in the mine. These dykes are regional features and are of the order of 50 to 90 feet wide, are almost vertical and cut all other rocks, including the ore.

Structure

The porphyritic rhyolite and the rhyolite breccia are folded into a broad anticline the axis of which strikes N 80°W. Further crossfolding on an approximate north-south axis has produced a domal effect on the original anticline. This doming is the major factor in the localization of the ore. As a result of the doming the contact between the porphyritic rhyolite and the rhyolite breccia dip off to the west, to the north and to the east, with small local variations in the attitude of the contact caused by smaller structures superposed on the larger structure. The south flank of the dome is truncated by the Horne Creek fault (Fig. 1B). On the Quemont property this fault strikes east and dips 82° south. Just south of the fault lies an assemblage of metadiabase, andesite and rhyolite breccia. Exact movement on the fault is not known although the regional north-south diabase dyke has been displaced across the fault 700 feet, north side east. The Donalda fault, a smaller subsidiary, branches off the Horne Creek fault in the mine area and is of some importance in interpreting structures within the mine.

The sequence of events as interpreted from the geology in the mine is as follows (Campbell, 1963):

1. Deposition of non-porphyritic rhyolite breccia and rhyolites.
2. Deposition of porphyritic rhyolite and andesite.
3. Folding and faulting of volcanic rocks.
4. Emplacement of ore.
5. Intrusion of diorites.
6. Emplacement of granitic intrusives.
7. Emplacement of diabase dykes.

Recurrent movement along faults has occurred since initial faulting. Post-ore and post diabase dyke faulting occurred in the mine.

Ore Bodies

As stated above the ore occurs in the rhyolite breccia at or near the contact of the breccia with the porphyritic rhyolite. Since this contact is conformable with the irregular domal structure present, the ore is located on the west, north and east flanks of the dome and also at the top or crest of the structure.

The sulphide ore bodies occur for the most part as massive sulphides, but some disseminated sulphides are present. Chloritization in variable amounts occurs at the margins of the ore. The ore consists of pyrite, pyrrhotite, sphalerite and chalcopyrite with some magnetite and electrum. Galena is present in very small quantities in one location in the mine.

In most areas of the mine pyrrhotite and pyrite are the predominating sulphides, these two minerals are intimately associated with each other in the ore bodies. Sphalerite and chalcopyrite are found in much smaller quantities in fractures and stringers within the massive pyrrhotite - pyrite bodies. On the average, chalcopyrite and sphalerite form about 13 percent by weight of the ore minerals (McLachlan et al. 1954).

Texturally the ore exhibits considerable variation. In some localities the pyrite cubes distributed throughout the massive pyrrhotite are as large as 1 1/2 cubic inches. Generally speaking, the large pyrite crystals are uncommon. Some localities exhibit intimate mixtures of sphalerite, fine grained pyrite and pyrrhotite. Others, show intimate mixtures of chalcopyrite and fine grained pyrite with very little pyrrhotite. For the most part the chalcopyrite occurs as filling in small vein like fractures and as a coating around larger pyrite crystals in massive pyrrhotite. The paragenetic sequence as obtained by the study of polished sections is the normal sequence of pyrite, pyrrhotite, sphalerite and chalcopyrite (Campbell, 1963). Campbell (ibid) believes this to be the order in which the minerals crystallized from a sulphide melt of certain bulk composition, rather than the order of introduction of the mineral species into a mineralized zone. Evidence obtained from this study agrees with this hypothesis.

EXPERIMENTAL WORK

Mass Spectrometry

Sulphur isotope ratios were determined on a twelve inch 90° , magnetic analyzer mass spectrometer built by Dr. H. R. Krouse of the Department of Physics, University of Alberta. The mass spectrometer is adaptable both to gas source and solid source work. All samples were burned to SO_2 and analyzed as such in the mass spectrometer. The mass spectrometer was equipped for simultaneous collection of mass 66 and mass 64. Mass 66 is $\text{S}^{34}\text{O}^{16}\text{O}^{16}$ and mass 64 is $\text{S}^{32}\text{O}^{16}\text{O}^{16}$. Correction factors for other combinations of S and O which give mass 66 are discussed later.

In the operation of the mass spectrometer the SO_2 gas was ionized by a stable electron beam at the source end. The individual ions were separated according to their masses in the magnetic field and the currents from these were collected in a double slit collector assembly and amplified by two vibrating reed electrometers. In the earlier part of this analysis (summer of 1964) a portion of the voltage of the larger ion current was fed back inversely by a calibrated five figure potentiometer to cancel the voltage developed by the smaller ion current. The null was then recorded with a centre-zeroed pen recorder. The reading obtained from the potentiometer at the null condition was then recorded. The number so obtained was directly proportional to the $\text{S}^{34}/\text{S}^{32}$ ratio depending on the amplification of the two ion currents.

In later analyses (1965) new equipment had been incorporated into the measuring circuit of the mass spectrometer. This included an integrating digital voltmeter, a voltage to frequency converter and a digital recorder. The application of this equipment to mass spectrometry is discussed in detail by McCullough and Krouse (1965). The basic operating principal of this equipment is that the integrating digital voltmeter integrates the input voltage over a selected period of time, and converts this voltage to a proportional frequency. Generally this frequency is referred to a standard time base frequency but in this circuit another voltage-to-frequency con-

verter is used in place of the standard time base so that the recorded voltage is actually a ratio of the two input voltages. In this case, the two input voltages are those of the ion currents of mass 66 and mass 64. The ratios are displayed visually on the voltage-to-frequency converter and may be printed out by the digital recorder at any desired time.

In both the more conventional circuiting method and in the newer method, accurate comparison of the mass 66 to mass 64 ratios of a known standard and an unknown sample was made possible by rapid sample switching with the use of a magnetic valve.

In the analysis for this study, SO_2 from a commercial cylinder was used as a secondary standard. The ratio of $\text{S}^{32}/\text{S}^{34}$ was found to be 22.17 or a δS^{34} value of 1.78.

In the analysis of each sample ten mass 66/mass 64 ratios of the secondary standard were recorded in a time lapse of approximately 15 seconds, then the samples were switched and ten mass 66/ mass 64 ratios of the unknown sample were recorded. This procedure was repeated until six sets of ratios for the standard and six sets of ratios for the unknown were recorded. The total time for this procedure was approximately one half hour. The ratios for each set were then averaged. This resulted in a number of mass 66/ mass 64 ratios for the standard (R_{std}) and a number of ratios of mass 66/ mass 64 for the unknown (R_x). These ratios were then compared. The final result was a mean average of R_x/R_{std} . All the results of this study are presented in terms of δS^{34} , that is, parts per thousand above or below the value of the meteoritic ratio of $\text{S}^{32}/\text{S}^{34}$. The ratio of $\text{S}^{32}/\text{S}^{34}$ for meteoritic sulphur is taken as 22.21. A more rigorous definition of δS^{34} is as follows:

$$\delta \text{S}^{34} \text{ ‰} = \frac{(\text{S}^{34}/\text{S}^{32})_x - \text{S}^{34}/\text{S}^{32}_{\text{std}}}{(\text{S}^{34}/\text{S}^{32})_{\text{std}}} \times 1000$$

The relationship between S^{34}/S^{32} ratios and mass 66/mass 64 ratios is:

$$\delta S^{34} = F \cdot \frac{R_x - R_{std}}{R_{std}} \times 1000$$

where F = correction factor for O^{18}

and R = mass 66/mass 64

In this study a value of 1.095 was used for F . This correction factor is to allow for the contribution to mass 66 by $S^{32}O^{16}O^{18}$. The effect of $S^{33}O^{17}O^{16}$ and $S^{32}O^{17}O^{17}$ is considered negligible. Other correction factors were found necessary in order to obtain the required degree of accuracy. A "leak factor" correction was found necessary since the glass capillary leaks through which the standard and the unknown samples passed were found to differ. No corrections were necessary for pressure, since both the standard SO^2 and the unknown sample were kept at the same pressure when readings were being taken. A "time correction" was also applied to all ratios. This compensated for any change in composition of the standard with time or for any drift in the electronics. In order to make this correction it was necessary to run a standard at the beginning and at the end of each day and to record times at which all ratios were obtained. To check the consistency of this "drift", in a number of runs the standard was analyzed between the first and last runs. In most cases when this was done the deviation of the standard from the line of drift was within .1 parts per thousand. All results of the mass spectrometer analysis are listed in table 1. Figure 2 shows the distribution of the sulphur isotopes in the mine.

Sample Preparation and Burning

All minerals were separated manually. A binocular microscope was used where necessary. In some cases a small electric drill was used in cutting up hand samples and in picking out small amounts of certain minerals from larger hand samples. The separated minerals were crushed in an agate mortar before burning.

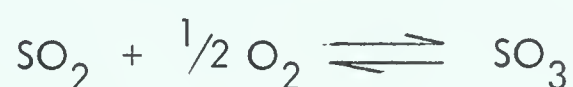
The samples were burned in a glass combustion train. This train consisted

essentially of a mullite tube, a quartz tube and a series of pyrex U-tubes and coils which were used in the SO_2 purification process. The furnace was heated electrically to a temperature of 1200°C , the temperature being kept constant to within ± 5 degrees by a temperature regulator and a platinum-rhodium wire thermocouple.

The samples were burned to SO_2 in the quartz tubing in a stream of pure tank oxygen. The oxygen was purified by passing it through Ascarite (a sodium hydrate asbestos absorbent) and then through concentrated H_2SO_4 . It was then passed through a heated mullite tube to oxidize any impurities left in the oxygen and then through a dry-ice trap, where these impurities might be trapped out. After this process it was allowed into the quartz combustion chamber where the sample was burned to SO_2 . Samples were slid in and out of the combustion chamber on small quartz boats.

The SO_2 was collected in liquid oxygen traps. This process also traps some excess oxygen as well as some contaminants. The excess oxygen is removed by pumping with vacuum pumps while the SO_2 is still frozen. The SO_2 is then warmed and the process repeated. Water is removed from the SO_2 sample by passing the gas three or four times through a trap cooled by a dry ice-acetone bath. The CO_2 in the dry SO_2 sample is removed by trapping the SO_2 in a trap cooled by ethyl-alcohol at its melting point (-117.3°C) and pumping off the CO_2 . The vapor pressure of the CO_2 at this temperature is about 800 times that of the SO_2 . Fractionation due to this process is taken to be negligible. After the CO_2 is removed, the SO_2 is transferred into a break-seal and collected.

A temperature of 1200°C was used in the burning process since at this temperature the equilibrium constant for the reaction



is very small and practically no SO_3 is produced. According to Rice-Jones (1953) the theoretical yield of SO_2 at 1200°C at equilibrium with SO_3 in a large excess of oxygen is 96.8%. This is favourable since there is a tendency at low temperature for the SO_3 to become enriched in the light sulphur isotope. Such an effect would alter the true

isotope ratios if the burning was carried out at a lower temperature. Higher burning temperatures were not used in order to increase the life time of the quartz tube.

Most of the samples were burned directly. Early in this study six samples of pyrite and pyrrhotite were burned after being converted to Ag_2S , and also directly as the pure mineral. It was found that in all cases the δS^{34} values obtained for the samples burned as silver sulphide, and the δS^{34} values obtained when the mineral was burned directly did not differ more than 0.1 δ . Because of this conversion to Ag_2S was considered unnecessary. The method that was used in converting the minerals to Ag_2S is listed in Appendix A.

TABLE 1a

 δS^{34} VALUES OBTAINED FROM PYRITE SAMPLES

<u>Sample</u>		<u>Level</u>	<u>Date</u>	$\delta \text{ ‰}$	<u>Precision</u>	$\delta \text{ ‰}$ <u>Av. Value</u>	<u>Mean deviation</u> <u>from average</u>
QO	Pyrite	200'	Aug. 10/64	.90	$\pm .15$.90	
Q1A	Pyrite	above		1.42	$\pm .18$		
Q1B	"	200'	Jan. 8/65	1.31	$\pm .25$	1.41	$\pm .07$
Q1C	"	level		1.51	$\pm .08$		
Q5	Pyrite	320'	Aug. 8/64	1.30	$\pm .16$.97	$\pm .33$
Q5	"	320'	Aug. 24/64	.64	$\pm .09$		
Q10	Pyrite	440'	Jan. 15/65	.99	$\pm .08$		
Q10	"	440'	Aug. 24/64	.34	$\pm .12$.70	$\pm .21$
Q10	"	440'	Aug. 8/65	.84	$\pm .16$		
Q10	"	440'	Jan. 18/65	.63	$\pm .24$		
Q14	"	900'	Aug. 10/64	.29	$\pm .25$.29	
Q15	"	1080'	Aug. 10/64	.79	$\pm .17$.85	$\pm .06$
Q15	"	1080'	Jan. 18/65	.91	$\pm .24$		
Q16	"	1260'	Feb. 11/65	.77	$\pm .12$.77	
Q20	"	1440'	Aug. 18/64	1.42	$\pm .15$	1.42	
Q28	"	1620'	Jan. 15/65	1.16	$\pm .15$	1.16	
Q33	"	1800'	Aug. 18/64	1.12	$\pm .22$	1.12	
Q61	"	1980'	Aug. 18/64	1.56	$\pm .16$	1.56	
Q37	"	2160'	Aug. 18/64	1.73	$\pm .13$	1.73	
Q40	"	2340	Aug. 18/64	1.38	$\pm .14$	1.38	
Q63	"	2520	Jan. 15/65	1.45	$\pm .30$		
Q45	"	2520	Aug. 10/64	1.15	$\pm .09$	1.30	$\pm .15$
Q46	"	2620	Aug. 19/64	1.52	$\pm .30$	1.52	
Q51	"	2820	Aug. 10/64	1.25	$\pm .15$	1.25	
Q55	"	2970	Aug. 24/64	1.76	$\pm .12$	1.76	
Q58	Pyrite	3120	Aug. 24/64	1.83	$\pm .10$		
Q58	"	3120	Jan. 15/65	2.00	$\pm .16$	1.82	$\pm .12$
Q58	"	3120	Jan. 18/65	1.64	$\pm .09$		

TABLE 1b

 δS^{34} VALUES OBTAINED FOR PYRRHOTITE SAMPLES

<u>Sample</u>	<u>Level</u>	<u>Date</u>	$\delta \text{‰}$	<u>Precision</u>	$\delta \text{‰}$ <u>Av. Value</u>	<u>Mean deviation from average</u>
Q 8 Pyrrhotite	320'	Aug. 24/64	.20	+.13	.15	+.08
Q 8 "		Aug. 8/64	.09	$\pm .07$		
Q10 "	440'	Aug. 8/64	.74	+.09	.68	+.07
Q10 "		Aug. 8/64	.73	$\pm .16$		
Q10 "		Aug. 10/64	.58	$\pm .16$		
Q15 "	1080'	Feb. 1/65	1.05	$\pm .14$	1.05	
Q16 "	1260'	Feb. 1/65	1.31	$\pm .12$	1.31	
Q23 "	1440'	Feb. 1/65	.78	$\pm .10$.78	
Q32 "	1800'	Feb. 11/65	.72	$\pm .07$.72	
Q37 "	2160'	Feb. 11/65	1.68	$\pm .13$	1.68	
Q45 "	2520'	Feb. 1/65	1.19	$\pm .15$	1.19	
Q51 "	2820'	Feb. 1/65	1.04	$\pm .11$	1.04	

TABLE 1c

 δS^{34} VALUES OBTAINED FOR SPHALERITE SAMPLES

<u>Sample</u>	<u>Level</u>	<u>Date</u>	$\delta \text{‰}$	<u>Precision</u>	$\delta \text{‰}$ <u>Av. Value</u>	<u>Mean deviation from average</u>
Q 1 Sphalerite	200'	Jan. 14/65	.73	+.17	.63	
Q 4 "	200'	Jan. 14/65	.52	$\pm .09$		
Q 2 "	200'	Jan. 18/65	1.28	$\pm .18$	1.28	
Q14 "	900'	Jan. 14/65	.43	$\pm .24$.43	
Q26 "	1620'	Jan. 14/65	.05	$\pm .17$.05	
Q44 "	2520'	Jan. 14/65	.89	$\pm .17$.89	
Q46 "	2620'	Jan. 14/65	.42	$\pm .14$.42	

TABLE 1d

 δS^{34} VALUES OBTAINED FOR CHALCOPYRITE SAMPLES

<u>Sample</u>	<u>Level</u>	<u>Date</u>	$\delta \text{ ‰}$	<u>Precision</u>	$\delta \text{ ‰}$ <u>Av. Value</u>	<u>Mean deviation from average</u>
Q 0 Chalco	200'	Aug. 24/64	+ .30	$\pm .10$	+ .30	
Q16 "	1260'	Feb. 10/65	+ .70	$\pm .18$	+ .62	$\pm .08$
Q16 "		Aug. 19/64	+ .53	$\pm .17$		
Q27 "	1620'	Aug. 19/64	- .18	$\pm .17$	+ .09	$\pm .26$
Q27 "		Feb. 11/65	+ .35	$\pm .07$		
Q40 "	2340'	Aug. 19/64	- .29	$\pm .15$	+ .17	$\pm .45$
Q40 "		Feb. 10/65	+ .61	$\pm .10$		
Q64 "	2620'	Feb. 10/65	+ .93	$\pm .09$	+ .93	
Q51 "	2820'	Feb. 10/65	+ .81	$\pm .13$	+ .81	

(Chalco = Chalcopryrite)

DISCUSSION OF RESULTS

The first most noticeable characteristic of the sulphur isotope ratios obtained in this study is the fact that all of the averaged values lie between 0 δ units and 1.82 δ units or between an S^{32}/S^{34} ratio of 22.21 and 22.17. This very small range of values is very similar to results obtained by Thode et al. (1962) in their study of the sulphur isotope abundances of the Sudbury district. It should be noted here that the writer did have four results which did not lie within this range. These "anomalous" results were discarded on the grounds that they were not reproduceable in two of the cases and the other two results were obtained at a time when instabilities in the mass spectrometer were strongly suspected. The writer regrets the fact that a shortage of time did not allow repetitions of the runs. As a result pyrrhotites Q58 and Q55 are not considered in this discussion but the writer does not completely dismiss the possibility that the values obtained for these samples were the correct ones. At the most this would increase the range of values obtained from $-.4$ to 2.2 δ units, which would still be a very small spread.

Kulp, et al. (1956) indicated that sulphur isotope ratios of ore deposits depend chiefly on source and listed a number of sulphur isotope ratios of ore deposits which were classed as magmatic sulphides. The following table is taken from their paper:

Pyrrhotites from Magmatic Sources

<u>Location</u>	<u>S^{32}/S^{34}</u>
Frood mine, Sudbury, Ont.	22.18
Rodgers Mine, St. Stephen, N.B.	22.23
Union Me	22.23
Marie Pond	22.22
Dracut Mass	22.42
Iron Mtn. Katahdin Me	22.73
Katahdin Iron Works Me	$22.82 \pm .08$

The authors note further that the first four sulphur isotope ratios listed are close to the meteoritic value and all are associated with mafic or ultramafic rocks which

may have been derived from the mantle. It is assumed here that the authors at this point were inferring that the sulphur in these samples may have come from the mantle since they state later that the sulphur in the latter three samples was "probably not derived solely from the mantle." The writer is of the opinion then that this must mean that Kulp and his co-workers believed sulphur could be brought up from the mantle with little or no change in its original isotopic composition and that the isotopic composition of sulphur in the mantle is close to or equal to that of meteorites. This idea is not inconceivable as is shown by the use of model lead ages. The assumption that lead is brought up from the mantle and into the crust without any change in isotopic composition due either to contamination or other factors, is used in the explanation of the isotopic composition of "ordinary lead", and is the basis on which dating of this lead is done. If this idea is acceptable, then it should not be unreasonable to think that sulphur may also under certain circumstances be brought up from the mantle and into the crust with no change in isotopic composition due to contamination. Granted, for this to occur certain ideal conditions would have to be present and for this reason the number of sulphide deposits in which the sulphur ratios are characteristic of the mantle should be small in comparison to the number of sulphide deposits in which the sulphur isotopic composition does show evidence of contamination. Now this is precisely what is observed if we accept the sulphur isotopic composition of meteorites as being representative of the sulphur composition of the mantle. That is, there are only a few deposits noted to date, which give a sulphur isotopic abundance close to the value of 22.21 for the ratio of S^{32}/S^{34} .

It follows from the above discussion that sulphur from galenas which give ordinary lead ages should usually give a S^{32}/S^{34} ratio close to or equal to that of the meteoritic value. The conformable-type lead deposits of Stanton et al. (1959) may not follow this hypothesis for obvious reasons. The assumption that the lead isotopic abundance in meteorites is equal to the lead isotopic abundance in the mantle has been tested

by Patterson (1955), (1956), and Chow and Patterson (1959) with a great degree of success and this seems to give further evidence that in all probability the sulphur isotope abundance in meteorites should also be representative of the sulphur isotopic abundance in the mantle.

Empirical evidence is limited but comparison of ordinary lead with sulphur isotope ratios and comparison of anomalous leads with sulphur isotope ratios seems to give support to this hypothesis.

The following sixteen sulphur ratios were quoted by Ault and Kulp (1960):

<u>Location and Sample</u>	<u>S^{32}/S^{34}</u>	<u>$S \text{ ‰}$</u>
Southern Rhodesia	(3 billion year old normal leads)	
HG 206	22.15	+2.7
HG 207	22.14	+3.2
HP 27	22.14	+3.2
HG 211	22.20	+ .4
Finland	(2 billion year old normal leads)	
HG 253	22.23	- .9
HG 260	22.14	+3.2
HG 262	22.27	-2.7
HG 259	22.26	-2.3
HG 264	22.40	-8.6
A 48	22.23	- .9
Sunshine Mine	(1 billion year old normal lead)	
"	22.14	+3.2
"	22.09	+5.4
Peru	(Fairly recent normal leads)	
	22.22	- .5
	22.24	-1.4
	22.12	+4.1
	22.25	-2.0

It is very apparent that the above data do show a tight grouping close to the meteoritic value. The average of the sixteen results is 22.20. Only one sample H.G. 264 from Finland falls much beyond the range of ± 5 δ units. It seems quite likely from this then that S^{32}/S^{34} ratios of galenas with ordinary leads should fall within this range. The S^{32}/S^{34} ratios of sulphides from deposits which show anomalous leads are usually scattered over a much wider range and are far from the meteoritic ratio of S^{32}/S^{34} .

Examples of this type of behaviour come from samples from Mississippi Valley and Ivigtut, Greenland. Kanasewich (1962) found Ivigtut leads to be anomalous. The S^{32}/S^{34} ratios from Ivigtut, Greenland, showed groupings around 22.10 and 22.50 (Ault, et al. 1960).

Considering the S^{32}/S^{34} values obtained from the Quemont mine, one would expect to find ordinary leads along with these sulphur ratios. Kanasewich (1962) has done lead ages on samples from Noranda and his work does show that the lead from Noranda can be considered ordinary. Noranda mine is only a very short distance from Quemont.

From the above discussion, it is concluded that the Quemont ore deposit is derived directly from the mantle or from a source in contact with the mantle. Emplacement of the ore body probably took place as a magmatic sulphide since under these conditions of emplacement the possibility of contamination of the sulphur would be negligible.

The idea that fractionation of sulphur isotopes may take place as a result of the crystallization of different minerals from a sulphide melt or from dilute solutions has been present in the literature for some time. MacNamara et al. (1952) stated that the ratio of S^{32}/S^{34} should show any isotopic fractionation that occurs due to the crystallization of a sulphide melt.

Vinogradov et al. (1956) in a discussion on sulphide minerals from a single deposit stated that:

"it may be assumed in further attempts one will detect differences in the ratios of the isotopes of sulphur in different minerals, distinguished from one another in temperature of crystallization for example in the series: pyrite, pyrrhotite, chalcopyrite, galena, etc."

Jensen (1957) lists sulphur ratios from apparently sequentially deposited minerals which show that the sulphur ratios do vary consistently in at least some specimens. This may indicate fractionation due to crystallization from hydrothermal solutions.

Work by other people, has not been too encouraging. Gavelin et al. (1960) found in their study of two Swedish ore bodies (the Boliden and the Falun) that no significant variation was noticeable when the early mineralization stage and the late mineralization stage were compared. It should be noted here that the deviation quoted on individual values of S^{32}/S^{34} was of the order of $\pm .7\%$. This would make it difficult to distinguish any small variations.

Ault, and Kulp, (1960) stated that there appeared to be no appreciable fractionation of sulphur isotopes during crystallization of ore. Their definition of appreciable was greater than $\pm .02$ of the S^{32}/S^{34} ratio.

In considering the crystallization of a melt, one would expect the first-formed mineral species to be relatively enriched in the heavy sulphur isotope (S^{34}). The mineral species which crystallizes in the last stages of crystallization of the melt would be expected to be relatively enriched in the lighter isotope (S^{32}). This could be explained as a result of the differences in vibrational energies of the two isotopes, that is S^{32} and S^{34} . The lighter isotope with the higher vibrational energy would in all probability prefer the liquid phase to the solid phase, and similarly the heavy isotope with the lower vibrational energy in all probability would prefer the solid phase to the liquid.

In the investigation carried out by the writer, the results of fractionation due to the above mentioned process are observable. The sequence of crystallization dealt with in this study is pyrrhotite and pyrite, sphalerite and chalcopyrite.

Figure 4 shows the separation between the averages of the combined pyrite

SULPHUR ISOTOPE DISTRIBUTION VS DEPTH

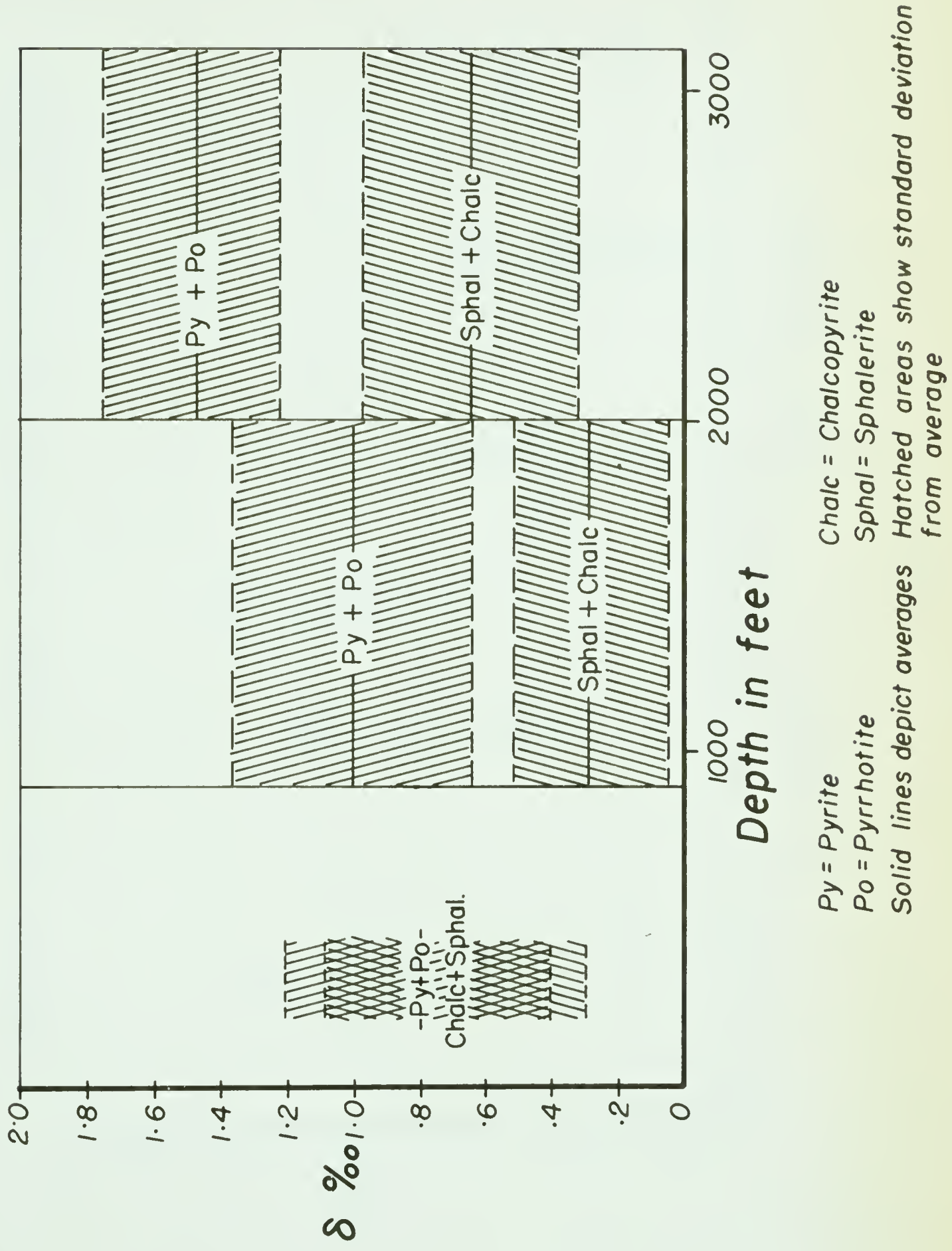


Fig. 3.

GRAPH SHOWING AVERAGE δ VALUES FOR VARIOUS MINERALS

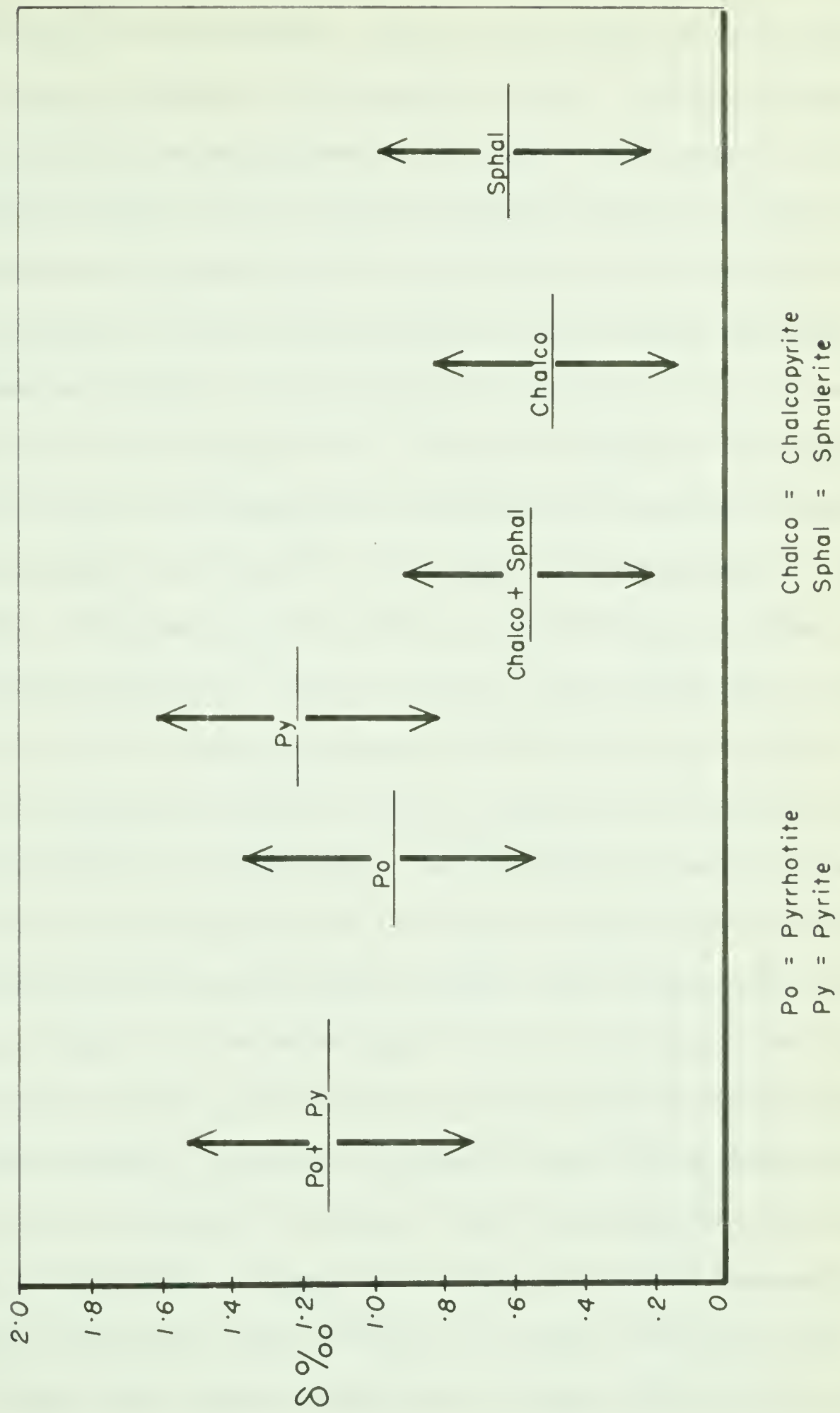


Fig. 4.

and pyrrhotite S^{32}/S^{34} ratios and the average of the combined chalcopyrite and sphalerite S^{32}/S^{34} ratios. As will be noted in this diagram there is some overlap when the standard deviations are considered. Figure 3 on the other hand shows a distinct and definite separation between the two groups of minerals. Furthermore Figure 4 gives some indication of separation between individual mineral species. This is almost pure speculation on the writer's part since the separation between the pyrite and the chalcopyrite ratios are too small to be of any significance with the present statistics. Such small differences, if real, may even be due to mineral lattice preference.

Returning to Figure 3 it is obvious that the separation is not quite as evident in the upper part of the ore deposit as it is in the lower 2,000 feet. The writer would like to point out that all the samples from the 900 foot level and lower are taken from a continuous ore body (see Figure 1B). In this paper this is designated as the south-west ore body. All the samples from the 440 foot level and higher are taken from the upper ore bodies (see Figure 1B). The south-west ore body and the upper ore body are not continuous and for this reason the break at the 900 foot level is indicated in Figure 3. In this figure the southwest ore body is separated into two portions, each approximately 1000 feet in vertical extent, for convenience in showing the trend in the results. The reason for the large overlap in the upper ore body as seen from Figure 3, is probably partly due to the small number of samples which was analyzed from this part of the ore deposit. It is the writer's opinion that if more samples from this part of the deposit were analyzed, a more evident separation would be realized between the two groups of minerals. At present no geological reason can be offered for this large overlap or for the apparent "anomalous" results of such samples as sphalerite Q2 and pyrrhotite Q8 (Table 1, Figure 2). It is fully realized that there may be many local variations within such a large ore deposit, and these variations may seem significant if only a small number of samples were analyzed. On the other hand the local variations may prove negligible if a large number of samples are used.

Considering the south-west ore body, the average separation between the two groups of minerals is of the order of $.8\text{‰}$. Although this amount is quite small it is considered significant, in fact, it is almost within the range which is considered "appreciable" by Ault and Kulp (1960). Their definition of appreciable as quoted previously was $\pm .02$ of the S^{32}/S^{34} ratio, which is approximately $.9\text{‰}$.

In considering the magnitude of the fractionation observed, one should keep in mind that most of the melt crystallized at a temperature above 540°C which is the crystallizing temperature of the sphalerite (Campbell, 1963). Therefore a large degree of fractionation would not be expected.

The writer therefore postulates that the ore formed by crystallization from a sulphide melt. Because the pyrrhotite and pyrite crystals formed first, they are relatively enriched in the heavy isotope of sulphur, and because the sphalerite and the chalcopyrite formed last, from a residual melt relatively enriched in the light isotope they show enrichment in the light isotope of sulphur. The residual liquid which was the source of the sphalerite and chalcopyrite probably remained in the liquid state for some time after the crystallization of the pyrrhotite and pyrite, thus permitting it to enter into fractures and fissures and to become situated along grain boundaries.

The general similarity of the S^{32}/S^{34} ratios of the pyrrhotites and the pyrite samples shows that the ore deposit in its crystallizing sequence is behaving as would be expected. From the binary phase diagram of the Fe-S system it is seen that it is not unreasonable to have the pyrite and the pyrrhotite crystallizing at or almost at the same time. From this it follows that the melt probably crystallized through very conventional means. It therefore appears reasonable that fractionation of sulphur isotopes due to crystallization of a sulphide melt does take place in a sequence of minerals formed at different temperatures.

Another significant feature of the results obtained is the small but steady enrichment of S^{34} in the samples with depth. This is quite noticeable from either Figure 3 or from Figure 5. Figure 5 is a plot of only the pyrite and pyrrhotite samples

SULPHUR ISOTOPE DISTRIBUTION WITH DEPTH

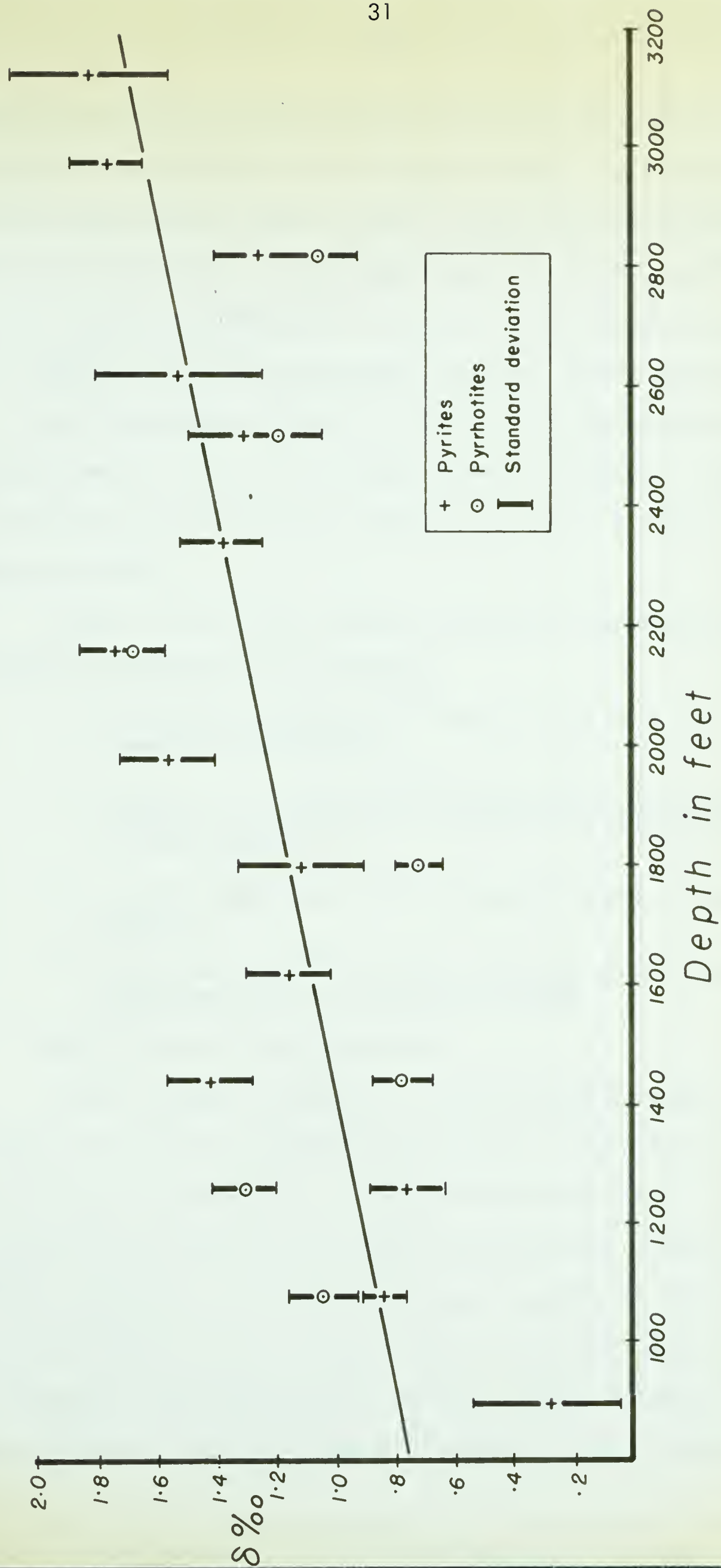


Fig. 5.

versus depth and only samples from the southwest ore body were used for the graph. The same relation is not noticeable within the upper ore body. This is as expected since only a very few samples from the upper ore body were examined and these come from a very small vertical extent of ore. It is noticed, though, that the average S^{32}/S^{34} ratio of the pyrite and pyrrhotite samples from the upper ore body is slightly lower than the upper 1,000 feet of the south-west ore body. However, this may not be significant.

Upon examination of Figure 5, it is noticed that the enrichment of the heavy isotope with depth is $.8\text{‰}$ for an increase in depth of 2,000 feet. This value is taken from the best fit curve for all points in Figure 11. The curve was drawn by the least mean squares method.

In order to arrive at any conclusions regarding an explanation for this trend, the following possibilities must be considered:

1. The relative enrichment of S^{34} with depth is a result of some type of crystallization phenomena.
2. The relative enrichment of S^{34} with depth is the direct result of a difference in load pressure between the bottom of the deposit and the top of the deposit.
3. The relative enrichment of S^{34} with depth is due to a normal geothermal gradient.
4. The enrichment of S^{34} with depth is the result of an abnormal geothermal gradient caused by an intrusive body at depth.

Each of these will be evaluated below.

In order to explain enrichment in the heavy isotope with depth in an ore body as a result of some type of crystallization phenomena, one would have to invoke either gravity settling or crystallization of the deposit from the bottom up. At present there is no reason for advocating that the ore body crystallized from the bottom up so this possibility is discarded. In enrichment due to gravity settling the first crystals to form would be enriched in the heavy isotope. If these crystals slowly settle to the base of the sulphide melt, the solidified product would be relatively enriched in the heavy isotope with depth. This process could in all probability result in a depth trend very

similar to the one observed in this study. Usually gravity settling produces some type of layering effect or other types of structures which may be taken as evidence of the occurrence of this process. In the Quemont deposit there is no evidence whatsoever for this, and on this basis this possibility is discarded.

Enrichment due to load pressure:

There is a possibility that fractionation may occur in sulphur isotopes because of a steep pressure gradient. That is, the light isotope of sulphur (S^{32}) may diffuse down the pressure gradient relatively faster than the heavy isotope (S^{34}) leaving a relative enrichment of S^{34} behind in areas of higher pressure. In a study of sulphur isotopes in the Yellowknife district, Wanless et al. (1960) showed that the lighter isotope had apparently migrated down the pressure gradient. Their pressure differences were very large and there was also a chemical potential gradient which probably aided in the migration of the light sulphur isotope. In the Quemont deposit, neither of these two factors apply. The pressure gradient is only approximately 20 bars and there is essentially no chemical potential gradient. The writer therefore dismisses this possibility on the basis that the process would be in-operative under the conditions present at Quemont.

Enrichment due to normal geothermal gradient:

It seems highly unlikely that the normal geothermal gradient would cause fractionation of sulphur isotopes within an ore body of such small vertical extent. The average "normal" geothermal gradient is generally twenty to thirty degrees centigrade for a depth of one kilometer. This value is for the upper three or four kilometers and the gradient is generally thought to decrease at depths greater than this. Considering the geothermal gradient to be the higher value quoted above ($30^{\circ}\text{C}/\text{km}$) the change in temperature within a vertical depth of 2,000 feet would be approximately 20°C . The batholiths or stocks in the same area as the Quemont

ore deposit are thought to be emplaced in the mesozone (Buddington, 1959). So it might be inferred from this that the ore body also was emplaced in the mesozone. This would put the ore originally at a depth of 6 to 8 miles from the surface which would mean a lower geothermal gradient under normal conditions. From this it is assumed that the maximum temperature difference along the vertical extent of the ore body would not be greater than 20°C under normal geothermal conditions and therefore insufficient to cause fractionation or differential migration of the sulphur isotopes.

Enrichment due to an abnormal geothermal gradient because of an intrusive body at depth:

If one looks at the general geology of the area, a number of small igneous bodies, the Powell granite, the Lake Dufault granodiorite and the Flavrian Lake granite are quite noticeable. The close spacing of these small intrusive bodies suggests a larger common parent intrusive at depth. Mining company personnel in the area consider this to be the case. Campbell (1962) has stated that the granites are post ore. Therefore there is a possibility that the thermal effect from such a mass at depth upon an already emplaced and solidified ore body might be sufficient to cause some fractionation of the sulphur isotopes within the ore body. The main effect would be to drive a relatively greater amount of the light isotope (S^{32}) than heavy isotope (S^{34}) away from the source of heat to cooler areas. This would leave that part of the ore body closest to the source of heat relatively enriched in the heavy isotope (S^{34}).

The following discussion is an attempt to look at this possibility from a somewhat less speculative point of view.

It is known that a "granitic" intrusive mass lies approximately two hundred feet below the ore body in the Quemont mine. This granitic intrusive is actually an alaskite, 80% quartz and alkali feldspar with minor mafics. In an attempt to deter-

mine whether or not this intrusive could produce a large thermal effect in the area, it was decided to use minimum temperatures in the following calculations. Thus the temperature of the intrusive "granite" is taken as 700°C.

To maintain a temperature as low as this the melt must contain approximately 10% water. This is not unreasonable since the surrounding country rock is not dehydrated to any great extent, and there are zones of chlorite rich rocks within the near vicinity which means the granite must have contained a fair amount of water. Another important consideration in this regard is the confining pressure. As stated above (Buddington, *ibid*), the small plutons which are exposed in the area were emplaced in the mesozone, that is at a depth of about 7 miles. With this in mind it is not unreasonable to assume that at the time of emplacement the "granitic" intrusion was under a pressure of three kilobars. At this pressure the intrusive body could hold the required amount of water and thus be molten at a temperature of 700°C (Goranson, 1938).

Ingersoll and Zobel (1913), and Lovering (1936) arrived at formulae for deriving contact temperatures. The following is from Ingersoll and Zobel (1913) and is a formula for the calculation of the contact temperature when the temperature of the intrusive and the initial temperature of the wall rock is known.

$$\theta_{ct} = \frac{\frac{\theta_o k_1}{h_1} + \frac{\theta_2 k_2}{h_2}}{\frac{k_1}{h_1} + \frac{k_2}{h_2}}$$

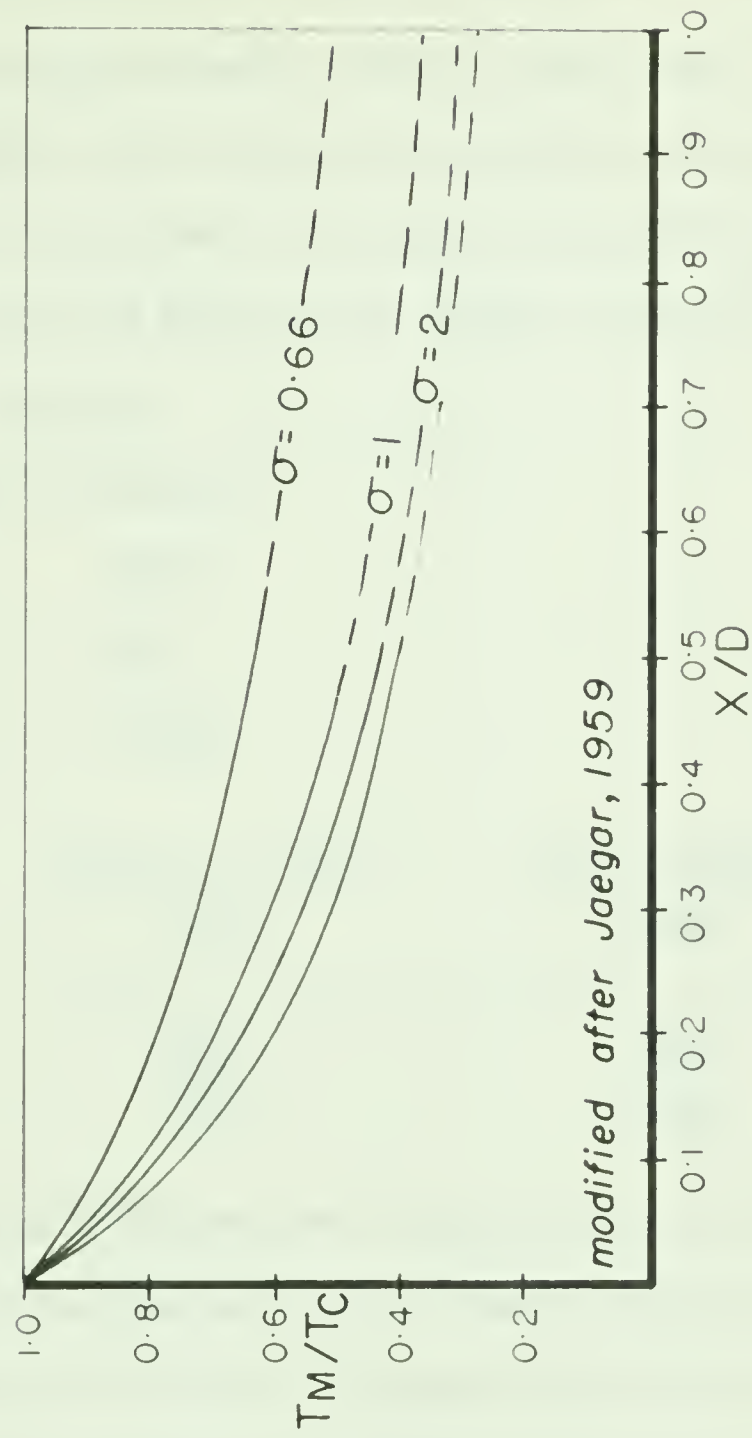
Where

θ_{ct} = contact temperature

θ_o = temperature of the intrusive body

θ_2 = initial temperature of the country rock

k_1 = thermal conductivity of intrusive



The ratio of the maximum temperature T_M attained at distance X from the margin of a sheet of thickness D to the initial contact temperature

Fig. 6.

k_2 = thermal conductivity of country rock

h_1 = the square of the diffusivity of the intrusive rock

h_2 = the square of the diffusivity of the country rock

In the following calculation the temperature of the country rock before the intrusive activity took place is taken to be 300°C. This seems to be a reasonable estimate since we are assuming a depth of emplacement of approximately seven miles. Using values for k and h obtained from a table presented by Lovering (ibid) and assuming the intrusive body to be similar to a granite porphyry, the following calculation gives a value of 539°C for the contact temperature.

<u>Intrusive</u>		<u>Country Rock</u>
(granite porphyry)		(Rhyolite)
$k_1 = .0057$		$k_2 = .0036$
$h_1 = .095$		$h_2 = .0888$
$\theta_1 = 700^\circ\text{C}$		$\theta_2 = 300^\circ\text{C}$

$$\theta_{ct} = \frac{\frac{700 \times 5.7 \times 10^{-3}}{.095} + \frac{300 \times .0036}{.0888}}{\frac{.0057}{.095} + \frac{.0036}{.0888}} = 539^\circ\text{C}$$

Jaegar (1959) presented a graph showing the ratio of maximum temperature at a distance x from the margin of an intrusive sheet of thickness D to the initial contact temperature (see Fig. 6). This graph was derived for an intrusive sheet but if the granitic body is considered to be planar on the upper surface, this graph could be used to approximate the maximum temperature attained at any distance away from the contact. Thus with a contact temperature of 539°C and on the assumption that the granitic body approximates an intrusive sheet between 2,000 and 4,000 feet thick, the temperature 200 feet away from the contact would be 430°C if the intrusive were

2,000 feet thick and 485°C if the intrusive were 4,000 feet thick. These values were obtained by using $\alpha = 1.5$. The value for α was calculated using the following formula given by Jaegar (ibid).

$$\alpha = \frac{K_1 h_o}{k_o h_1}$$

<u>Intrusive</u>	<u>Country Rock</u>
(Granite Porphyry)	(Rhyolite)
$k_1 = .0057$	$k_o = .0036$
$h_1 = .095$	$h_o = .0888$

$$\alpha = \frac{5.7 \times 8.88 \times 10^{-5}}{3.6 \times 9.5 \times 10^{-5}} = 1.48$$

Using the same value of α , the temperature 2,000 feet from the contact of the intrusive would be approximately 180°C for a sheet 2,000 feet thick and 250°C assuming a thickness of 4,000 feet for the intrusive. From these calculations it is seen that there will be an approximate temperature difference of at least 200°C between the two extreme ends of the ore deposit. It should be noted here, however, that the values obtained for temperatures at the two extreme ends of the ore deposit were all based on a α of 1.5. This value does vary with the type of rock through which the heat flows. Jaegar (1959) notes that with decreasing ratio of the conductivity of the country rock to that of the intrusion, the maximum temperatures at any distance x from the intrusion falls off more rapidly. But the thermal conductivity of the ore body on the whole is probably higher than that of the surrounding country rock, therefore a temperature drop of 200°C may be too high.

Therefore to show that a large difference in temperature could still be obtained between the top and the bottom of the ore deposit, it is necessary to determine the changes in the above calculations when the thermal constants for a pyrite-pyrrhotite rich ore body are used.

The thermal conductivity of pyrite as determined by Horai (1963) is 7.22×10^{-3} cal./cm sec °C and that of pyrrhotite is 8.62×10^{-3} cal./cm sec °C. (Uyeda and Horai, 1963). Campbell (1963) stated that the composition of the Quemont ore in terms of iron sulphides recalculated to 100 percent is 44 mole percent pyrite and 56 mole percent pyrrhotite. Weighting the pyrite and the pyrrhotite thermal conductivities, the average thermal conductivity of the ore is found to be 8.0×10^{-3} cal./cm. sec °C. Similarly by calculation the mean density of the ore was found to be 4.81 gm/cm^3 and a value of .135 cal/gm/°C for the specific heat of FeS was obtained from the Handbook of Chemistry and Physics. This value is used as an approximate figure in the following calculation. In the calculation of the diffusivity the following equation was used:

$$h^2 = \frac{k}{cp}$$

where h^2 = diffusivity

k = thermal conductivity = 8.0×10^{-3} cal/cm sec °C

c = specific heat = .135 cal/gm/°C

p = density = 4.81 gm/cm^3

From this $h^2 = .0123$ and therefore $h = .110$ in c.g.s. units.

α is then calculated as follows:

$$\alpha = \frac{k_1 h_o}{k_o h_1}$$

Intrusive body
(granite porphyry)

k_1 = .0057

h_1 = .095

Country Rock
(pyrite-pyrrhotite ore)

k_o = .008

h_o = .110

$$\alpha = \frac{5.7 \times 1.1 \times 10^{-4}}{8 \times .95 \times 10^{-4}} = .825$$

It is found that for many non-metallic materials the diffusivity is constant for changes in temperature and therefore it is assumed here that the diffusivity will not vary

appreciably. The conductivity on the other hand will vary with changes in temperature but since the conductivity for non-metallic materials usually increases with an increase in temperature and since for metallic minerals it will usually decrease with an increase in temperature, the net effect will probably be a slight increase in the value for α . Because of this the writer thinks that the maximum range for α is from 1.5 to .825 and in all probability the correct value lies closer to 1.5 than to .825. From Fig. 6 it is obvious that changes in α within this range will not change the differences in temperature between any two points to any great degree. Therefore a temperature difference of 200°C between the bottom and the top of the southwest ore body does not appear to be unreasonable. Although the ore body is a mass of metallic sulphides for which the conductivity might be quite high, it must be remembered that it is quite different from just a standing column of metallic sulphides. Its shape is the shape of a melt which has squeezed its way into its present position, bulging here and then thinning out there as it was injected into faults and fractures. Furthermore the ore itself is intruded by other dioritic and rhyolitic bodies. It seems that when one takes these factors into consideration it is quite reasonable to assume that the conductivity of the ore deposit on the whole is not much more than the surrounding country rock, and therefore α will be approximately 1.5.

Following the above discussion it is believed reasonable that the enrichment of the S^{34} isotope with depth observed in this study is a direct result of the emplacement of the granitic intrusion after the ore body was in place and already solidified. Added evidence in favour of this hypothesis is the fact that chalcopyrite samples Q51 and Q64 are enriched in the heavy isotope of sulphur relative to the other chalcopyrite samples although they are lighter than the pyrite and pyrrhotites of the same level. (See Figure 2 and Table 1). Both these samples come from a rhyolite dyke zone in the mine. It is thought that the heat effect from the dykes has enriched the chalcopyrite in the heavier isotope of sulphur. The pyrite sample Q46, which is on the same level is unaffected by this because it is from a location away from

the rhyolite dykes. It is noticed that all Q51 samples show a relatively close grouping. Since Q51 samples are from a dyke zone, the grouping effect seen is a result of partial homogenization of the sulphur isotopic compositions of these sulphides. The net effect has been to enrich the chalcopyrite in the heavier isotope, and the pyrite and pyrrhotite in the lighter isotope. This explains why the samples from the 2820' level in Figure 6 appears below the normal trend. Although a minimum temperature was used for the intrusive, higher temperatures will not affect the net result greatly. It should also be noted that the formula used for calculating contact temperatures is one with which one must assume immediate emplacement of the intrusive. The net effect of having a more slowly moving intrusive emplaced would be to raise the contact temperature. The same effect is again obtained when one includes the latent heat of crystallization in the calculations. The raising or lowering of the contact temperature, or even moderate changes in value for α , will not greatly affect the results. The main purpose of the calculations was not to show absolute temperatures at certain points away from the intrusive but to show that there could well be a significant difference in the maximum temperature attained at the bottom and at the top of the ore body.

In conclusion it seems reasonable to think that the sulphide melt and the "granitic" intrusive were originally both differentiates of a magma of mantle derivation or of a source in direct contact with the mantle. The immiscible sulphide separated from the granite at an early stage, probably in the very early stages of intrusion. When the immiscible sulphide separated from the granite, it was immediately brought up and into its present position within the mesozone. The country rocks had already been deformed at this stage. The large change in conditions (pressures and temperatures) allowed the escape of volatiles including some sulphur in the form of H_2S . The sulphur which escaped at this time was probably enriched in the light isotope, thereby leaving the ore deposit slightly enriched in the heavy isotope of sulphur. Because of the high temperature at this time the amount of fractionation would be small, and since the melt would still be in the liquid state, isotopic equili-

bration within the melt would occur. Later as crystallization commenced Rayleigh fractionation took place because of liquid-solid fractionation tendencies. Some time after solidification of the sulphide melt the granite worked its way up into its present position. The outward flow of heat from the intrusive brought about a significant temperature change (as discussed previously) in the ore body, probably raising the temperature of the ore body 200°C higher at the bottom than at the top. Because of this temperature gradient, differential migration of the light sulphur isotope (S^{32}) took place down the temperature gradient thus leaving the lower part of the deposit relatively enriched in the heavy isotope. Later, isotopic equilibration did not take place because of the lack of some type of activation energy needed to start the process.

It seems quite probable that the whole sequence of events that is indicated by the geology of the area is a result of one orogeny as stated by Campbell (1963). This includes the extrusion of the lavas, the folding and the faulting, the emplacement of the ore and other minor intrusives and the final event, the emplacement of the mesozonal stocks of the area. This process may have taken somewhere in the order of 300 million years to complete.

APPENDIX A

PROCEDURE FOR CONVERTING SULPHIDE ORE SAMPLES TO Ag_2S 1. Procedure for obtaining BaSO_4

1. Grind adequate amount of sample in agate mortar.
2. Weigh an amount of ore equivalent to at least 25 mg BaSO_4 , but not exceeding 300 mg BaSO_4 and transfer to a dry 600 ml beaker.
3. Add 10-15 ml concentrated HNO_3 and 2-3 ml liquid bromine, let stand over night.
4. Heat gently on not too hot steam bath till all bromine vapors are gone. Now evaporate to dryness on steam bath.
5. Add 10 ml concentrated HCl and evaporate to dryness again. Repeat with another 10 ml HCl .
6. If any dark-coloured ore particles remain undissolved, repeat 3, 4 and 5.
7. Add 25 ml distilled water, 2 ml HCl . If appreciable amounts of insoluble matter are present at this stage, filter through a #541 filter paper and evaporate again to dryness (600 ml beaker). Dissolve in 25 ml H_2O and 2 ml HCl .
8. Heat on flame till just boiling, add 20 ml concentrated ammonia, keep boiling for 60 seconds and put beaker on steam bath for only a couple of minutes before filtering.
9. Filter through a #541 filter paper into a 600 ml beaker, wash thoroughly with hot distilled water for many times (total of filtrate about 400 ml).
10. Add 3 drops of methyl orange as an indicator and neutralize with concentrated HCl . Add $1/2$ to 1 ml HCl in excess. Bring volume to about 500 ml. Put boiling rod in beaker.
11. Bring to boil. Add 10 ml of a boiling 10% BaCl_2 solution. Keep gently boiling so as to maintain a steady circulation in the supernatant liquid. As soon as all turbidity is gone (usually 20 to 45 min.) the BaSO_4 precipitate is ready to filter.
12. Filter BaSO_4 through a #40 filter paper. Wash 5 times with cold distilled water.
13. Ignite filter plus BaSO_4 in quartz crucible using small Bunsen flame as long as carbon is still present in contact with BaSO_4 . Heat subsequently with Meker burner, but only for a couple of minutes.
14. In those cases where dark ore particles remain undissolved in HNO_3/Br_2 mixture, make sure that these particles do not contain sulphur by using the $\text{Na}_2\text{O}_2 - \text{Na}_2\text{CO}_3$ fusion method on the residue of the filtration sub. 7.

II. Preparation of SO_2 samples starting from BaSO_4

1. Reduction of BaSO_4

BaSO_4 is reduced to H_2S by a boiling mixture of HI, H_3PO_2 and HCl. The active reducing agent is HI. The hypophosphorous acid will reduce free I_2 back to HI.

Composition of the reducing mixture:

500 ml (=850 g) HI ($d = 1.7$)

816 ml concentrated HCl

245 ml H_3PO_2 50%

When preparing this mixture, care has to be taken to remove any sulphur compounds present in any of the components (especially the hypophosphorous acid) by simply boiling it for approximately 45 minutes. This will expel any sulphur present as H_2S . Before using this mixture for reductions it is advisable to make a blank run for each batch of reducing mixture prepared, to make sure that the mixture is actually free from sulphur.

The reduction is carried out in a 200 ml round bottom flask provided with a reflux cooler. The H_2S formed is flushed out with a nitrogen stream, washed with distilled water and absorbed in a Cd-acetate solution of the following composition:

62.5 g Cd-acetate

500 ml acetic acid 17N

2000 ml distilled water

Washing of the H_2S with distilled water is a necessity to prevent contamination of the Cd-acetate absorbent with chlorides. The reduction is carried out over a period of about one hour. If conducted properly, the reduction is quantitative. A rule of the thumb is to use 100 ml of reducing mixture for each 200 mg BaSO_4 .

2. Conversion of CdS to Ag_2S

CdS is converted to Ag_2S by adding 0.1 N AgNO_3 . In case yield measure-

ments are required, one has to add standardized AgNO_3 from a burette for the back titration of excess AgNO_3 with NH_4CNS . As a rule this will not be necessary and approximately 20 ml AgNO_3 is added for each 100 mg of BaSO_4 reduced. To get the Ag_2S in a form easy to filter, the mixture has to be heated before filtration to coagulate the Ag_2S . The quickest way is to heat on a burner flame until boiling and to continue boiling for one minute. Under this condition the Ag_2S is very easy to filter over glass wool. The Ag_2S precipitate is washed twice with concentrated ammonia (to remove any AgCl present) and after that with distilled water. No more than traces of AgCl should be visible in the filtrate after washing with ammonia. If appreciable amounts of AgCl show up, the reduction procedure should be checked. The Ag_2S is dried in an oven at about 100°C .

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SULPHUR ISOTOPE DISTRIBUTION IN THE QUEMONT ORE DEPOSIT

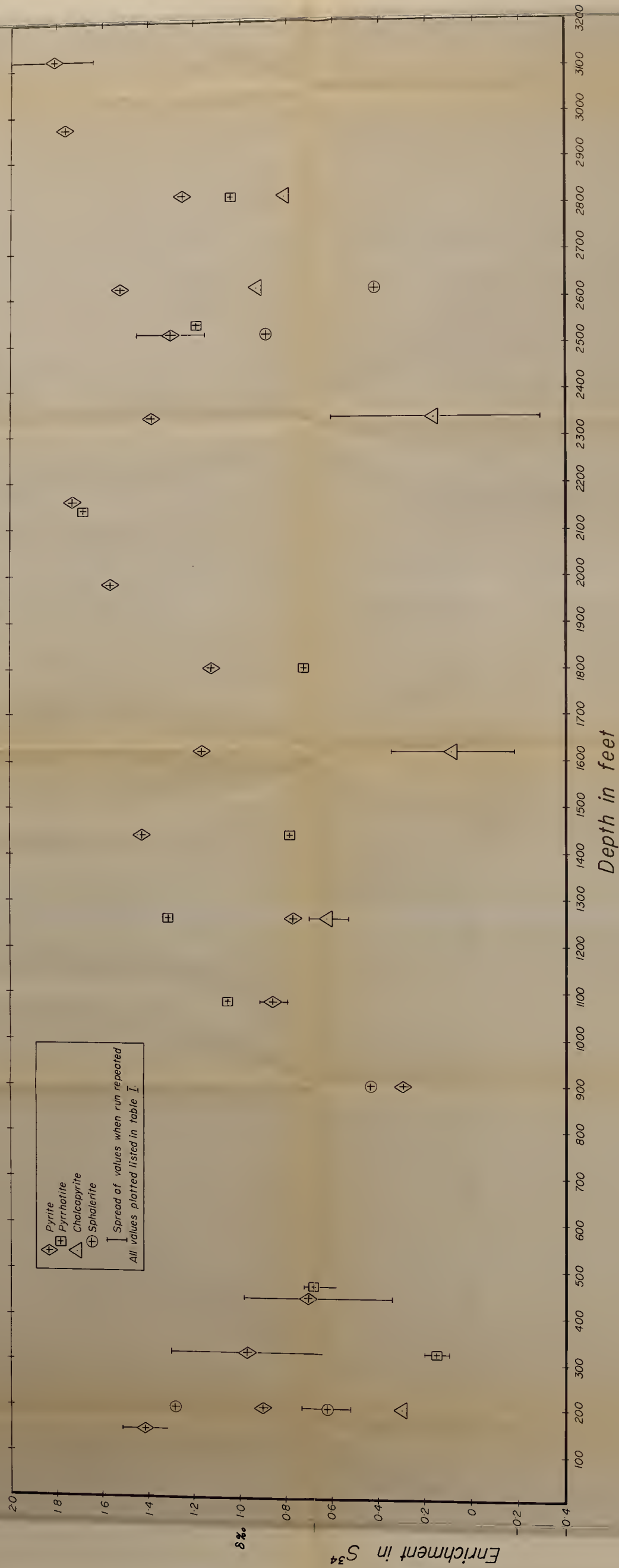


FIG. 2.

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